Polyhedron 154 (2018) 430-435

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Methyl viologen iodobismuthates

Petr A. Buikin^{a,b}, Andrey B. Ilyukhin^a, Nikolai P. Simonenko^a, Veronika K. Laurinavichyute^c, Vitalii Yu. Kotov^{a,b,d,*}

^a N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation ^b Higher Chemical College RAS, D. I. Mendeleev University of Chemical Technology of Russia, 125047 Moscow, Russian Federation ^c Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation ^d National Research University Higher School of Economics, 101000, Moscow, Russian Federation

ABSTRACT

[BiI₅]/SiO₂ composite material.

ARTICLE INFO

Article history: Received 23 May 2018 Accepted 7 August 2018 Available online 18 August 2018

Keywords: Bismuth complexes Optical band gap Crystal structure Thermal stability Methyl viologen

1. Introduction

In recent years, the chemistry of organic-inorganic hybrid halobismuthates has attracted growing attention in advanced materials studies. This interest was inspired by promising physical properties inherent in this class of compounds, for example, semiconductivity, photochromism, luminescence, etc. Alkyl viologen halobismuthates are ones of the most popular halobismuthates [1–8]. Methyl viologen (Scheme 1) chlorobismuthates are remarkable for their photoinduced colour change, due to outer-sphere charge transfers [1,2]. Methyl viologen iodobismuthate [MV][Bil₅] [3], as well as the mixed methyl viologen chloro-iodo-bismuthate [MV][BiCl₂I₃] [4] and methyl viologen bromo-iodo-bismuthate [MV][BiBr_{3.8}I_{1.2}] [5] exhibit unusual spectral properties owing to the appearance of low-energy exciton bands in their spectra. Their appearance is usually associated with the presence of linear and quasilinear all trans-Bi-I-Bi-I chains in their crystal structures with Bi-I-Bi and I-Bi-I angles about 180°. Our quantum-chemical calculations on the electronic structure of 1,1'-(1,5-pentanediyl)bis(4methylpyridinium) iodobismuthate [9] demonstrated that the electronic transitions with the lowest energy in such compounds are $5p_v(I) \rightarrow 6p_v(Bi)$. Most of the methyl viologen halobismuthates, including [MV][Bil₅], were obtained by solvothermal synthesis in a

methanol solution. In the present work, we explored the possibility of the synthesis of $[MV][BiI_5]$ in water solutions and its deposition on SiO₂ substrates for further studies of its photophysical properties.

2. Results

2.1. Synthesis and X-ray diffraction study

The interaction of iodobismuthate anions and methyl viologen [MV]²⁺ cations in aqueous solutions led to

the formation of three compounds, two of which were identified as [MV][Bil₅] and [MV]₃[Bi₂]₁]I. Hybrid

iodobismuthates [MV]₃[Bi₂I₁₁]I and [MV]₃[Bi₂I₉]₂(DMF)₃(H₂O) were isolated from dimethylformamide

(DMF). The heating of the latter material (up to 200 °C) resulted in a mixture of products, one of which was identified as [MV][BiI₅] A simple antisolvent precipitation method was proposed to create the [MV]

The interaction of aqueous solutions of $[MV]I_2$ and potassium iodobismuthate (a mixed solution of KI and Bi(NO₃)₃) in the molar ratio of 1:2 ($[MV]^{2^+}$:Bi³⁺) results in the fast formation of a red precipitate (1) (Scheme 2). No colour change was observed for 1 in contact with the mother liquor solution over 24 h. Being separated from the reaction mixture, product 1 was found to be stable for a long time. The experimental XRD pattern of 1 (Fig. S5) and the calculated XRD pattern of [MV][BiI₅] [3] are different.

An increase in the $[MV]^{2+}$ to Bi³⁺ molar ratio up to 1:1 results in the fast formation of the red precipitate of **1** as well. However, in contact with the mother liquor solution the colour of the precipitate changes to black within a few minutes. The obtained compound can be identified as $[MV][BiI_5]$ [3] (Fig. S6 in the ESI). Details of the Rietveld refinement: space group P2₁, *a* = 6.4749 (3) Å, *b* = 15.4048(7) Å, *c* = 11.2597(5) Å, *β* = 101.116(3)°, *R*_{exp}: 4.04%, *R*_{wp}: 6.64%, *R*_p: 5.22%, GOF: 1.65. No colour change was observed for the black precipitate $[MV][BiI_5]$ in contact with the mother liquor solution over 24 h.







© 2018 Elsevier Ltd. All rights reserved.

^{*} Corresponding author at: N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. *E-mail address*: VYuKotov@gmail.com (V.Yu. Kotov).



Scheme 1. The molecular structure of the methyl viologen cation $([C_{12}H_{14}N_2]^{2\ast}$ or $[MV]^{2\ast}).$



Scheme 2. Synthesis of methyl viologen iodobismuthates.



Scheme 3. The molecular structure of the 1,1'-(hexane-1,6-diyl)bis(2-aminopyridinium) cation ($[C_{16}H_{24}N_4]^{2+}$ or [HBAP]²⁺).

In the reaction mixture with a molar ratio of $[MV]^{2+}$ to Bi³⁺ of 2:1 the initially formed red precipitate 1 turns into the black precipitate [MV][BiI₅] within a couple of minutes, and after another 10 min it turns into a dark red precipitate [MV]₃[Bi₂I₁₁]I (2). Further aging of 2 in the reaction solution does not lead to any visible changes in the system. Details of the Rietveld refinement for 2: space group P2₁, a = 16.103(1) Å, b = 32.246(2) Å, c = 11.5612(7) Å, $\beta = 90.00(4)^{\circ}$, R_{exp} : 3.74%, R_{wp} : 11.78%, R_p : 8.84%, GOF: 3.15. (Fig. S7 in the ESI). Recrystallization of 2 from DMF results in the formation of a crystalline product, however the crystals were not suitable for single crystal X-ray analysis. Details of the Rietveld refinement: space group P2₁, a = 16.102(1) Å, b = 32.267(1) Å, c = 11.5620(6) Å, $\beta = 89.98(2)^{\circ}$, R_{exp} : 4.67%, R_{wp} : 11.82%, R_{p} : 8.58%, GOF: 2.53. According to the results of the X-ray powder diffraction analysis, **1** and **2** are proved to be different phases (Fig. S5). However, the main product of crystallization of 1 under the hydrothermal conditions (140 °C, 20 h, aqueous solution of 5.6 M KI) was identified as 2. Details of the Rietveld refinement: space group P2₁, a = 16.092(1) Å, b = 32.252(1) Å, c = 11.5681(8) Å, $\beta = 90.000$ (3)°, R_{exp}: 4.94%, R_{wp}: 11.35%, R_p: 8.70%, GOF: 2.30. The crystals of 2 obtained by hydrothermal synthesis were found to be suitable for single crystal X-ray analysis.

Our crystallization attempts of **1** or $[MV][Bil_5]$ from DMF led to the formation of a coloured glass with inclusions of red crystals of $[MV]_3[Bi_2l_9]_2(DMF)_3(H_2O)$ (**3**). The pure form of this compound can

be obtained by removing the solvent from a mixed solution of [MV] I_2 and BiI₃ in DMF (with the molar ratio of [MV]I₂:BiI₃ of 3:4) in air. Details of the Rietveld refinement (without sample grinding, Fig. S8 in the ESI): space group $Cmc2_1$, a = 17.0275(7) Å, b = 34.723(1) Å, c = 14.8151(6) Å, R_{exp} : 1.20%, R_{wp} : 4.77%, R_p : 3.10% GOF: 3.98. The heating of compound 3 up to 143 °C leads to its decomposition with the loss of three DMF molecules and one H₂O molecule (Fig. S1d in the ESI, the theoretical mass loss is 6.05%, the experimental mass loss is 6.19%), and the formation of a black product. According to the X-ray powder diffraction data, this product contains a mixture of 1 and [MV][BiI₅] (Fig. S9 in the ESI). It should be note that compound **3** is subjected to a tribochemical reaction (similar to thermal decomposition) during the grinding. According to X-ray powder diffraction analysis, the ground crystals of 3 are contaminated by 1 and [MV][BiI₅] (Fig. S10 in the ESI). Details of the Rietveld refinement: space group $Cmc2_1$, a = 17.0378(9) Å, b = 34.834(1) Å, c = 14.8900(6) Å, R_{exp} : 6.31%, R_{wp} : 12.56%, R_{p} : 9.37%, GOF: 1.99.

It is noteworthy that the compound **2** contains $[Bi_2I_{11}]^{5-}$ anions, which has not been described previously [10]. According to previous work [11], the Bi:halogen ratio in the anion can be varied either by varying the reagent ratio in the reaction mixture or by adjusting the solution acidity. In our work we observed the formation of **2** when changing the reagent ratio in the reaction mixture from 1:1 to 2:1. The effect of acidity on the product composition can be illustrated for 1,1'-(hexane-1,6-diyl)bis(2-aminopyridinium) (HBAP, Scheme 3) halobismuthates. We demonstrated for the iodobismuthate system that low acidity promotes crystallization of [HBAP][BiI₄]₂·2H₂O (**4**), while high acidity (concentrated HI) facilitates the crystallization of [HBAP]₃(H₃O)₂[Bi₂I₁₁][BiI₆] ·6H₂O (**5**). One of the 1,1'-(hexane-1,6-diyl)bis(2-aminopyridinium) bromobismuthates [12] contains the similar $[Bi_2Br_{11}]^{5-}$ anion.

2.2. Single crystal X-ray analysis.

Crystal data for **2**. The structure of **2** is formed by $[MV]^{2+}$ cations, together with $[Bi_2I_{11}]^{5-}$ and I^- anions (Fig. 1a). The unit cell contains two crystallographically independent anions (both I^- anions are disordered over two positions) and six crystallographically independent cations. The torsion angle between adjacent aromatic rings varies from 12.4° to 32.7°. Ionic associates $[Bi_2I_{11}]_{2}^{10-}$ are formed by short $I(7)\cdots I(13')$ contacts (3.730 Å), while longer I (2) $\cdots I(18)$ contacts (3.925 Å) are responsible for the formation of a 1D-chain (Fig. 1b). If we approximate the chains as rods, the latter will form a dense packing structure (Fig. S2a in the ESI). The shortest $I\cdots I$ contacts between the nearest chains are larger than 4.2 Å. $[MV]^{2+}$ cations and I^- anions are located between the 1D-chains (Fig. S2 in the ESI).

Crystal data for **3**. The crystal structure of **3** contains $[MV]^{2+}$ cations, $[Bi_2I_9]^{3-}$ anions and solvate molecules of DMF and H₂O (Fig. 2 a, b). Both the crystallographically independent anions $[Bi_2-I_9]^{3-}$ and cations, containing the N(1) and N(2) atoms, have crystallographic symmetry *m*. Bridging I atoms in the anions lay in the plane *m*, where the plane *m* passes through the center of the bridging C–C bond in the cation, containing the N(1) atom, and finally, the plane *m* is perpendicular to the plane of the cation and passes through the atoms N(2,3) in the cation. Like all the solvate molecules, the cation containing the N(4) atom is disordered about the plane *m*. The shortest I···I contact in the structure of **3** is 4.183 Å.

Crystal data for **4**. The **s**tructure of compound **4** is formed by $[\text{HBAP}]^{2+}$ cations, 1D-chains of $[\text{BiL}]_n^{n-}$ (parallel to the c-axis) and solvent H₂O molecules (Fig. S4a in the ESI). The periodicity of the chain is 7.82 Å and this coincides with the value of the parameter *c*. The HBAP aliphatic fragment has the t-t-t-t-t conformation (the

Download English Version:

https://daneshyari.com/en/article/11006147

Download Persian Version:

https://daneshyari.com/article/11006147

Daneshyari.com